Concentrations of "legacy" and novel brominated flame retardants in matched samples of UK kitchen and living room/bedroom dust

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UNIVERSITY OF BIRMINGHAM

Cover Letter

21th Jan, 2016

Dear Dr. Myrto Petreas,

I am glad to receive the comments from the reviewers who have presented nice comments and suggestions to help improve the manuscript. All of the reviewers' comments have been responded point-by-point in the following pages. All modifications are shown in the annotated version of the revised manuscript by using track changes mode. The publication-ready version of the revised manuscript is also uploaded. I hope these modifications will make the manuscript suitable for publication in your journal.

I am very grateful to the reviewers for their attentive and detailed comments. I am also very grateful for your great time and effort for my manuscript!

If you have any question, do not hesitate to contact me.

Sincerely yours

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Response to comments to CHEM39301

Editor comments:

Both reviewers are in favor of a publication and I concurred that a minor revision from your part is necessary before a final decision. In particular, please provide more information on analytical methods and QC and explore the suggestion to present ratios of concentrations in different rooms.

Response:

Dear Editor,

Thank you very much for your comments on our manuscript entitled “Concentrations of "Legacy" and Novel Brominated Flame Retardants in matched samples of UK kitchen and living room/bedroom dust”. We have made corresponding changes to it according to the comments from reviewers which we found to be very constructive. More information on analytical methods and QC are provided in the response, and concentration ratios in different rooms are presented in the revised version.

Comments of Reviewer #1

General Remark

The Manuscript "Concentrations of "Legacy" and Novel Brominated Flame Retardants in matched samples of UK kitchen and living room/bedroom dust" was well written and I would recommend for publication.

Response:

Thank you very much for your recommendation. We have carefully considered your comments and have revised the manuscript accordingly.

Specific Comments

(1) Some details should be given about the vacuumed area (m^2) and the sampling time

Response: Vacuuming area and time is added in the manuscript, with the reader referred to further details about sampling in our previously published paper (Harrad et al., 2008).

(2) a. Was any EPA standard method followed regarding analytical condition on GCMS?

b. Were all the measured areas within the range of calibration curve?

c. The results have been corrected for recoveries?

d. Was the calibration level based on average RF, linear curve, other?

e. Was there more than one level in calibration curve?

Response: Thanks for this comment. Our responses to each of the sub-points follow:

a. We have not used a EPA standard method for the determination of PBDEs and NBFRs, and instead have used an in-house method.

b. In our method, the calibration range (20-1000 pg/µL) corresponds to a concentration range of 40-2000 ng/g in dust. This covers most data points, except for some extremely high concentrations of BDE-209, and some very low concentrations. As these outliers are very rare, we believe our method is fit-for-purpose.

c. As we use internal standards to calculate the concentration, the results are inherently corrected for recovery.

d. We prepared a 5-point calibration curve ranging from 20 pg/µL to 1000 pg/µL of native standards (together with 200 pg/µL of all internal and recovery determination standards in each) at the beginning of analysis to calculate the relative response factor (RRF). On a day-to-day basis, we conduct continuing calibration using a single calibration point (500 pg/µL native standards) run at the start and end of each sample batch. Quantification of samples in that batch is made using the average of the RRFs obtained for the two continuing calibration standards. As a QA/QC check, the RRFs obtained from each continuing calibration must fall within ±25% of the RRFs obtained in the initial 5-point calibration. If this criterion is not met, then a new full 5-point calibration must be run.

e. See our response to point d above.

(3) Please change chapter 3.2 format between right-aligned and left-aligned

Response: Thanks very much. We have revised this.

Reference

Harrad, S., Ibarra, C., Abdallah, M.A.-E., Boon, R., Neels, H., Covaci, A., 2008. Concentrations of brominated flame retardants in dust from United Kingdom cars, homes, and offices: Causes of variability and implications for human exposure. Environment International 34,

1170-1175.

Comments of Reviewer #2

General Remark

This manuscript reported the concentrations of "legacy" and novel brominated flame retardants (BFRs) in matched samples of UK kitchen and living room/bedroom dust. The temporal trend of BFRs and the difference between different microenvironment in house was investigated. This is a first study the contamination of BFRs in kitchen and the data of the present study is also valuable for us to further understand the indoor pollution and human exposure. This is a well-written paper containing interesting results which merit publication. A few minor revision are list below.

Response:

Thank you very much for your recommendation. We have carefully considered your comments and have revised the manuscript accordingly.

Specific Comments

(1) A comparison between the present study and previous studies was conducted twice, respectively in first section (Line 221-Line227) and the second section (3.2). What's the different between these two comparisons?

Response: Thanks very much for this comment. The comparison in the first section is intended to place our data in a general global context, as it compares median concentrations of kitchen and living room/bed room in this study with median concentrations reported in 25 previous studies. In these 25 previous studies, dust was not only collected from living rooms, but also from offices, classrooms, cars, airplanes, gyms etc. Also, these studies were not limited to the UK.

In contrast, the comparison in section 3.2 is specifically focused on testing the hypothesis that recent restrictions on PBDE manufacture and use have led to a decrease in PBDE concentrations and an increase in potential replacement NBFRs. To do so, it compares concentrations of target BFRs in living room/bedroom in this study with those reported in a previous study which investigated the same BFRs in living room dust from the same area of the UK taken a number of years previously.

(2) Line 16: "BDE-99 (2.6-1440 ng/g)" change to "BDE-99 (2.6-1,440 ng/g)" to consistent with others.

Response: Thanks. The text is revised accordingly.

(3) Line 18-20: "The concentrations in living rooms/bedrooms are at the lower end of those reported in previous UK studies." This conclusion is inaccuracy. In fact, only some of target exhibited lower levels than those in previous studies. As shown in figure 2 (Line 236-238), median levels of 9 out of 16 target BFRs in dust from living rooms/bedrooms in this study are comparable or to higher than those reported in previous UK studies. Moreover, this statement is inconsistent with the conclusion in Line 345-346 "Concentrations of 16 BFRs in dust from living rooms/bedrooms and kitchens from 30 UK homes are moderate compared with previous studies."

Response: Thank you very much to point this out. We revised the text in line 18-20 to "The concentrations in kitchens and living rooms/bedrooms are moderate compared with previous studies" so now it is consistent with experimental results and context.

(4) There were several written forms for PBDE congener, please unify the writing of PBDEs. For examples: "BDE-28, 47, 99, 100, 153, 154, 183 and 209" (line 109-110); "especially for BDEs-47, -154 and -153" (line 223).

Response: Thanks. We've unified this in the revised version.

(5) Line 45: Please unify the writing of "hexabromocyclododecane (HBCDD)".

Response: Thanks for this comment. The writing of HBCDD has been unified.

(6) Line 229-232 (Table 1): I would advise the authors included the ratios of concentrations of BFR in matched kitchen/living room (bedroom) dust, which make it more intuitive to comparable the levels between these two microenvironments.

Response: Thanks for this advice. K/L ratios have been added in the revised version.

Concentrations of "Legacy" and Novel Brominated Flame Retardants in matched samples of UK kitchen and living room/bedroom dust

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Abstract

Concentrations of polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDDs) and 5 novel brominated flame retardants (NBFRs) were measured in paired samples of kitchen and living room/bedroom dust sampled in 2015 from 30 UK homes. BDE-209 was most abundant (22–170,000 ng/g), followed by γ-HBCDD (1.7–21,000 ng/g), α-HBCDD (5.2–4,900 ng/g), β-HBCDD (2.3–1,600 ng/g), BDE-99 (2.6-1,440 ng/g), BDE-47 (0.4–940 ng/g), decabromodiphenyl ethane (DBDPE) (nd-680 ng/g) and bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEH-TEBP) (2.7-630 ng/g). The concentrations in kitchens and living rooms/bedrooms are moderate compared with previous studies. ~~at the lower end of those reported in previous UK studies.~~ Concentrations of BDE-209 in living room/bedroom dust were significantly lower and those of DBDPE significantly higher ($p<0.05$) compared to concentrations recorded in UK house dust in 2006 and 2007. This may reflect changes in UK usage of these BFRs. All target BFRs were present at higher concentrations in living rooms/bedrooms than kitchens. With the exception of BDE-28, pentabromoethylbenzene (PBEB) and DBDPE, these differences were significant ($p<0.05$). No specific source was found that could account for the higher concentrations in living rooms/bedrooms.

Keywords

Brominated flame retardant; dust; kitchen; living room; bedroom

Highlights

- First report of BFRs in domestic kitchen dust
- Levels of most BFRs significantly lower in kitchen than living room/bedroom dust
- Lower levels in kitchens may be due to more frequent cleaning and fewer BFR sources
- BDE-209 and DBDPE in house dust respectively decreased and increased since 2006-07

1. Introduction

In order to comply with flame retardancy regulations in many jurisdictions, flame retardants (FRs) are widely added to textiles, plastics and building materials. At the current time, brominated flame retardants (BFRs) remain the most widely used class of FRs across the world, including: polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDDs), tetrabromobisphenol A (TBBPA), decabromodiphenyl ethane (DBDPE) and 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) (Alaee et al., 2003; Covaci et al., 2011). To date, a number of studies have reported potential adverse human health impacts for some BFRs, including thyroid toxicity (Meerts et al., 2000), neurotoxicity (Dingemans et al., 2011), reproductive toxicity (Meeker et al., 2009) and carcinogenicity (Darnerud, 2003). In addition, BFRs like PBDEs and HBCDDs are persistent, bioaccumulative and capable of undergoing long range environmental transport (Dickhut et al., 2012; Marvin et al., 2011; Wu et al., 2011; Zhang et al., 2009; Zhu et al., 2013). Owing to emissions from the myriad range of goods within which they have been incorporated, BFRs are ubiquitous in the environment and have been detected in nearly all abiotic environmental compartments (including water, air, soil, sediments, sewage sludge and dust) (Besis and Samara, 2012; Cristale et al., 2013; Gorga et al., 2013; Luo et al., 2013; Zhu et al., 2008). Such contamination has led to the widespread presence of

BFRs in biota such as insects, birds and mammals (Gaylor et al., 2012; Guo et al., 2012; Jorundsdottir et al., 2013), as well as human tissues like hair, breast milk and blood serum (Aleksa et al., 2012; Kim and Oh, 2014; Lee et al., 2013; Sjödin et al., 2013; Tang et al., 2013).

Current understanding is that human exposure to PBDEs and HBCDDs occurs via a combination of diet, indoor dust ingestion, dermal exposure, and inhalation of (largely indoor) air (Abdallah et al., 2008; Besis and Samara, 2012; Daso et al., 2010; Johnson-Restrepo and Kannan, 2009; Trudel et al., 2011). The suspected ecological and human health risks of BFRs have driven international regulation of production and use of some. Specifically, the commercial Penta- and Octa-BDE formulations have been banned worldwide and listed under the UNEP Stockholm Convention on persistent organic pollutants (POPs) since 2009 (Ashton et al., 2009). Moreover, the commercial Deca-BDE formulation has also been restricted severely in Europe since July 2008 (European Court of Justice, 2008), and is currently under active consideration for listing under the Stockholm Convention. In addition, HBCDDs was listed under Annex A of the Stockholm Convention in 2013 (Report of COP6, Stockholm Convention, 2013). Such restrictions and bans on PBDEs and HBCDDs, when coupled with the fixed or even increasing market demand for flame retardants is inevitably leading to increased production of alternatives. While organophosphate flame retardants (PFRs) are one alternative, others include the so-called “novel” BFRs

(NBFRs) such as: DBDPE, BTBPE, pentabromoethylbenzene (PBEB), bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEH-TEBP) and 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB). However, despite their perceived low cost and high performance, there exist substantial concerns about the environmental impacts of these and other NBFRs. Combined with the substantial remaining inventory of goods containing banned (or "legacy") BFRs and their persistence in the environment, this increased use of NBFRs means that environmental concerns about BFRs will remain an important issue for a considerable time.

With respect to the contamination of indoor dust with BFRs, most attention has been paid to house dust, with offices, cars and schools also featuring in some studies (Harrad et al., 2010). Within homes, the majority of studies have examined living room dust, with a smaller proportion studying bedrooms. To our knowledge however, no data exist about concentrations of BFRs in dust from domestic kitchens. This is a surprising omission, given that people may spend a substantial proportion of time in this microenvironment, and that kitchens contain a substantial number of goods such as microwave ovens, dishwashers, food processors, fridges, and freezers etc. that because their plastic components represent a fuel source in the event of fire, are likely to be flame-retarded.

Given this background, the objectives of this study are: 1. to report for the first time the concentrations of selected BFRs in kitchen dust; 2. to test the hypothesis that concentrations of BFRs in domestic kitchen dust exceed those in dust sampled simultaneously from other areas (living rooms/bedrooms) in the same houses, and 3. to test the hypothesis that restrictions on PBDEs in the EU, have led to reductions in concentrations of PBDEs in dust from UK living rooms, accompanied by concomitant increases in concentrations of NBFRs.

To achieve these objectives, we determined concentrations of 8 PBDEs (BDEs-28, 47, 99, 100, 153, 154, 183 and 209), 5 NBFRs (PBEB, EH-TBB, BTBPE, BEH-TEBP and DBDPE) and HBCDDs (α-, β-, γ-) in paired UK kitchen and living room (or bedroom) dust samples taken from 30 homes in the UK West Midlands conurbation in 2015. Data from kitchens are compared with those from living rooms and bedrooms; with those from living rooms/bedrooms in this study compared with those recorded in an earlier study conducted by our research group of dust from living rooms sampled in the UK West Midlands conurbation in 2006-07.

2. Material and methods

2.1 Sampling

In total, 30 homes from the West Midlands conurbation in the UK (of which

Birmingham is the main city) were sampled in 2015. For each home, a dust sample from the kitchen floor was collected with a floor dust sample collected from the living room in the same house for comparison. For the 11 homes in which the living room and kitchen were in the same room, dust in the bedroom was collected instead. For carpeted floor, dust was collected by vacuuming ~~on~~ a 1 m^2 area for 2 min~~;~~ while~~and~~ for bare floors, the vacuuming area and time were 4 m^2 and 4 min, respectively. ~~An aliquot of 2-3 g pre-baked sodium sulfate was collected as field blank.~~ More details about ~~The~~ dust collection and storage protocols have been described in our previous studies (Harrad et al., 2008). An aliquot of 2-3 g pre-baked sodium sulfate vacuumed from a clean Al foil surface served~~was collected~~ as a field blank.

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2.2 Chemicals

Native BDEs 77 and 128, ^{13}C-BTBPE, ^{13}C-BEH-TEBP, ^{13}C-BDE-209 and ^{13}C- α-, β-, γ-HBCDDs were used as internal standards. All standards above were purchased from Wellington Laboratories Inc. All solvents used (acetone, hexane, iso-octane and methanol) were HPLC grade.

2.3 Clean-up

First, 50-100 mg dust was accurately weighed and spiked with 25 ng internal (surrogate) standards. Hexane : acetone (3:1) (2 mL) was added to the sample, which was vortexed for 60 seconds, sonicated for 5 min and centrifuged at 2000 g for 2 min.

After collecting the supernatant, the residues were subjected to the same extraction process twice more. The combined supernatants were reduced in volume to ~ 2 mL under a gentle stream of nitrogen gas, before mixing with 3-4 mL 98% sulfuric acid. The mixture was then vortexed for 20 s followed by centrifugation at 2000 g for 5 min. The supernatant was then collected. To ensure complete transfer, the residue was rinsed with hexane (2 mL) three times. The combined supernatant was then reduced to incipient dryness under a gentle stream of nitrogen gas. The final concentrate was re-dissolved in 200 µL iso-octane prior to analysis of PBDEs and NBFRs by GC-MS. Following GC-MS analysis, solvent exchange from iso-octane to methanol was conducted to facilitate determination of HBCDDs on LC-MS-MS.

2.4 Analytical methods

2.4.1 GC-MS

A Thermo Trace 1310 gas chromatography interfaced with an ISQ single quadrupole MS equipped with a programmable-temperature vaporiser (PTV) was employed to conduct the analysis under electron capture negative ionisation (ECNI) mode. Two µL of purified sample extract were injected on a Thermo TG-SQC column (15 m×0.25 mm×0.25 µm). The injection temperature was set at 92 °C, held 0.04 min, ramp 700 °C/min to 295 °C. The GC temperature programme was initially 50 °C, held 0.50 min, ramp 20 °C/min to 240 °C, held 5 min, ramp 5 °C/min to 270 °C and then ramp 20 °C/min to 305 °C, held 16 min. Helium was used as a carrier gas with a flow rate

of 1.5 mL/min for the first 22.00 min, then ramp 1.0 mL/min^2 to 2.5 mL/min, hold 13.00 min. The mass spectrometer was employed in selected ion monitoring (SIM) mode and the measured ions for each compound are listed in Table S1. Dwell times for each ion were 30 ms. The ion source and transfer line temperatures were set at 300 and 320 °C, respectively and the electron multiplier voltage was at 1400 V. Methane was used as reagent gas.

2.4.2 LC-MS-MS

A high-performance liquid chromatography (HPLC, LC-20AB, SHIMADZU) followed by electrospray ionisation and tandem mass spectrometry (ESI-MS-MS, API 2000, AB Sciex) was employed to measure the concentration of HBCDDs in this study. A Varian Pursuit XRS3 C18 analytical column (150 mm × 2 mm, 3 μm particle size) was used as stationary phase, and the mobile phase was a mixture of 1:1 water and methanol (phase A) and methanol (phase B). Elution started at 50 % phase B and then increased linearly to 100 % over 4 min, held isocratically for 5 min and then decreased to 65 % over 3 min, then returned to initial condition in 0.01 min and maintained for column regeneration for another 4 min, resulting in a total run time of 16 min. The flow rate and injection volume were 0.15 mL/min and 20 μL, respectively. The mass spectra were obtained in ESI (-) mode and data collected in MRM mode, with the parent and daughter ions for each compound listed in Table S2.

2.5 QA/QC

As a QA/QC check, one aliquot of SRM2585 (organics in house dust, NIST) was analysed for every 20 samples. Data obtained for these SRM analyses were very reproducible and in good agreement with the certified values (Table S3). One field blank was analysed every 10 samples. Most target compounds were not detected in blanks, or were detected at levels equivalent to a concentration in dust of below 1 ng/g, except BDE-209, which was detected in blanks at around 20 ng/g. Even for BDE-209, concentrations in blanks were always less than 5% of the concentrations detected in samples. Concentrations of each compound found in blanks are listed in Table S4 and are subtracted from the results of samples before further analysis of the data. The limits of detection for each target compound are listed in Table S5.

2.6 Statistical analysis

Statistical analysis of the data was conducted using Microsoft Excel 2013 to generate descriptive statistics, with all other statistical procedures conducted using IBM SPSS Statistics 19.0. As a first step, the distribution of concentrations of each compound within the dataset for each microenvironment category was evaluated using a Kolmogorov-Smirnov test. The results of this test and visual inspection of frequency diagrams together revealed both concentration and dust loading data in kitchen and living room to be log-normally distributed. Hence, concentrations and dust loadings

were log-transformed before performing t test comparisons. In all instances, where concentrations were below the detection limit, the concentration was assumed to equal half of the detection limit.

3. Results and discussion

3.1 Concentrations of BFRs

Table 1 lists minimum, maximum, and median concentrations of target BFRs in both kitchen and living room/bedroom dust in this study, while a boxplot (Figure 1) illustrates the concentration range and profile of target BFRs in our samples. Based on concentration range, the 16 BFRs targeted in this study may be categorised into three groups. BDE-28, PBEB, BDE-100, EH-TBB, BDE-154, BDE-153, BDE-183 and BTBPE belong to the first group, ranging from not detected to several tens ng/g with median concentrations lower than 10 ng/g. The second group contains BDE-47, BDE-99, BEH-TEBP, DBDPE and α-, β-, γ-HBCDDs, for which median concentrations range from 10 ng/g to hundreds ng/g and concentrations range from several ng/g to in excess of 1,000 ng/g. Finally, group 3 consists of BDE-209 only, for which concentrations range from several tens ng/g to more than 100,000 ng/g with a median value of nearly 1,000 ng/g. The concentration ranges and profiles obtained in this study are broadly consistent with previous studies as shown in Figure 2. This Figure plots median concentration values for exemplar previous studies (Abdallah et

al., 2008; Ali et al., 2013; Ali et al., 2012a; Ali et al., 2011; Ali et al., 2012b; Allen et al., 2013; Bjorklund et al., 2012; Brown et al., 2014; Carignan et al., 2013; Coakley et al., 2013; Dirtu et al., 2012; Dodson et al., 2012; Harrad and Abdallah, 2011; Harrad et al., 2008; Kalachova et al., 2012; Kang et al., 2011; Kefeni and Okonkwo, 2012; Nguyen Minh et al., 2013; Ni and Zeng, 2013; Shoeib et al., 2012; Stasinska et al., 2013; Tang et al., 2013; Thuresson et al., 2012; Vorkamp et al., 2011; Whitehead et al., 2013; Yu et al., 2012), alongside those detected in kitchen and living room/bedroom dust in this study (represented as red and black dots respectively). It can be seen that for most compounds, concentrations in this study are lower than previously reported, especially for BDEs-47, -154 and -153. This finding is not inconsistent with a reduction in the use of the Penta-BDE formulation since the early-mid-2000s. In contrast, concentrations of NBFRs, HBCDDs and BDE-209 recorded in this study are similar or even slightly higher than previously reported, which is consistent with the later introduction (or absence to date) of restrictions on use of these BFRs.

~~Table 1 Maximum, minimum and median concentrations of target BFRs in dust from kitchens (K) and living rooms/bedrooms (L), ng/g~~

	~~Maximum~~		~~Minimum~~		~~Median~~	
	~~K~~	~~L~~	~~K~~	~~L~~	~~K~~	~~L~~
~~BDE-28~~	~~150~~	~~55~~	~~<0.2~~	~~<0.2~~	~~1.2~~	~~1.0~~

BDE-47	940	590	0.4	2.4	7.6	13
BDE-99	1400	930	2.6	4.0	17	33
BDE-100	320	140	<0.2	0.7	1.7	3.2
BDE-153	410	170	0.1	<0.4	1.7	1.9
BDE-154	180	60	<0.4	<0.4	0.4	0.7
BDE-183	29	120	<1.0	0.6	1.9	4.2
BDE-209	32000	170000	22	170	590	1500
PBEB	25	15	<0.2	<0.2	0.3	0.4
EH-TBB	290	450	<0.2	<0.2	4.1	12
BTBPE	10	97	<1.0	<1.0	1.2	4.5
BEH-TEBP	420	630	2.7	7.8	36	75
DBDPE	450	680	<9.2	21	74	120
α-HBCDD	3800	4900	5.2	75	110	280
β-HBCDD	1100	1600	2.3	6.4	29	67
γ-HBCDD	13000	21000	1.7	14	35	110

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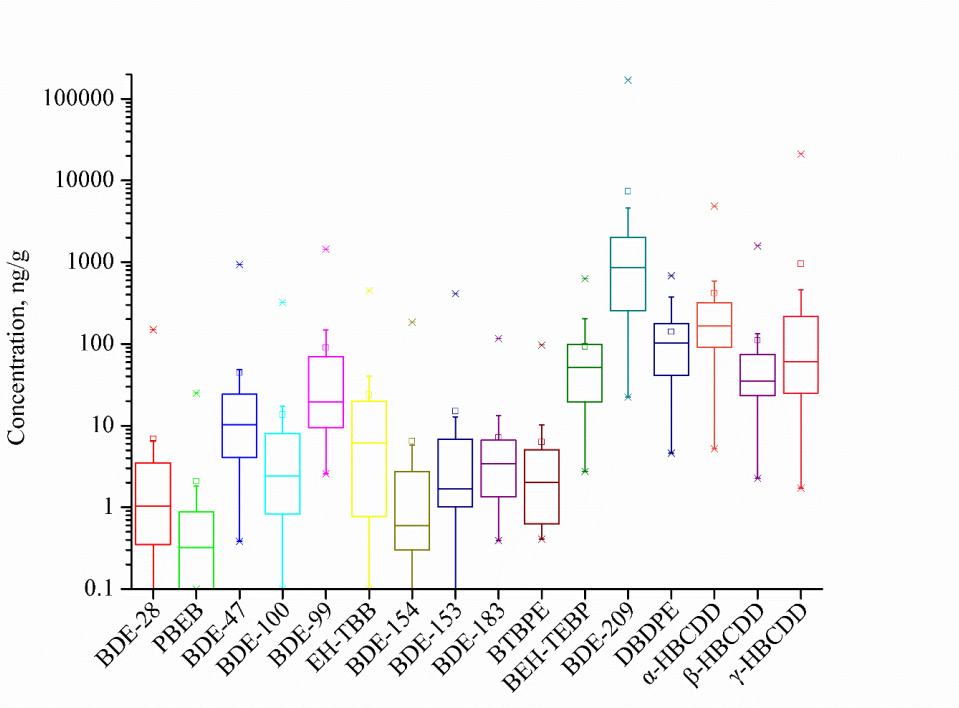
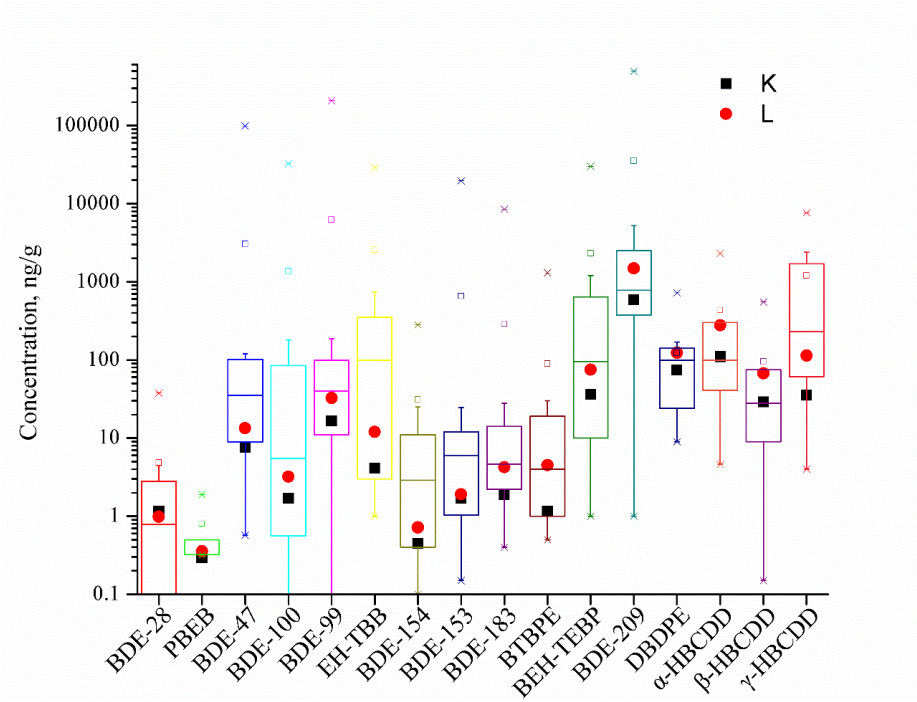


~~Figure 1 Concentration range of BFRs in this study~~



240

241 ~~Figure 2 Median concentrations of target BFRs in this study (K, kitchen; L, living room/bedroom) compared to the range of medians reported in~~

242 ~~selected previous studies~~

3.2 Is there evidence of temporal changes in BFR concentrations in living room/bedroom dust following restrictions on PBDE use?

To investigate the impact of recent restrictions on manufacture and use of PBDEs on concentrations of PBDEs and potential replacement NBFRs in UK indoor dust, we compared concentrations of individual PBDEs, BTBPE, and DBDPE in living room and bedroom dust in our study, with those reported for 30 UK living room dust samples collected between 2006 and 2007 (Harrad et al., 2008). Before doing so, we first conducted a t-test comparison of log-transformed concentrations of our target BFRs in our living room and bedroom dust samples to verify the validity of aggregating these data in this context. This revealed no significant differences ($p>0.05$) between concentrations in living room and bedroom dust for any of our target BFRs. Consequently, we compared BFR concentrations in living room dust from 2006-07 with our combined data for living room and bedroom dust via a t test comparison of log-transformed concentrations in the two temporally-distinct sample groups. This revealed concentrations of most target BFRs to be statistically indistinguishable ($p>0.05$) between the two time periods. However, concentrations of BDE-209 and BDE-154 are significantly lower ($p<0.05$) and those of DBDPE and BDE-28 significantly higher ($p<0.05$) in this (later) study. While it is hard to rationalise the opposite trends in BDEs-28 and -154, and acknowledging the small sample numbers involved; the apparent decrease in concentrations of BDE-209, coupled with the

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corresponding increase of DBDPE, is not inconsistent with the 2008 introduction of restrictions on use of Deca-BDE in the EU (European Court of Justice, 2008), and reports that DBDPE is the main alternative to Deca-BDE (Covaci et al., 2011).

3.3 Are concentrations of BFRs higher in kitchen than living room/bedroom dust?

To test our hypothesis that concentrations of BFRs in kitchen dust will exceed significantly those in living area and bedroom dust from the same homes, we conducted a paired t test comparison between concentrations of individual BFRs in kitchen dust and those in living room and bedroom dust. This revealed concentrations for all but BDE-28, PBEB, and DBDPE to be significantly higher ($p<0.05$) in living room and bedroom dust compared to that from kitchens. Moreover, although not significant ($p>0.05$), a higher concentration was still observed for BDE-28, PBEB and DBDPE in living room/bedroom dust compared to kitchen dust. The higher concentrations observed in living rooms and bedrooms compared to the corresponding kitchens are not attributable simply to the respective number of putative sources in the two microenvironments. Kitchens in this study contained more potential sources, such as: fridges, microwave oven, washing machines, ovens, toasters, and curtains etc. than living rooms/bedrooms (which contained mainly carpets, TVs, computers, sofas, and curtains). Instead, it is plausible that the goods present in kitchens are treated with FRs other than the BFRs targeted in this study, in contrast to the goods found in living

rooms/bedrooms. As carpet was absent from all the kitchens in this study, while being the most frequently reported putative source in living rooms/bedrooms (present in 21/30 of these microenvironments), we examined further whether the presence/absence of carpets in this study could explain the differences between kitchens and living rooms/bedrooms. To do so, we classified the 60 dust samples into 3 groups: i.e. kitchen samples (K), bare floor living room/bedroom samples (BL) and carpeted living room/bedroom samples (CL) and subjected data on BFR concentrations (in this instance not log-transformed) in samples in each of these groups to a Kruskal-Wallis test. However, the mean ranks of BL and CL are very close (Table 2) and both are much higher than those of kitchen samples for most compounds. This result indicates that the presence of carpet does not significantly influence the concentrations of our target BFRs in living room/bedroom dust. Hence, the absence of carpet from kitchens does not account for the lower concentrations compared to living rooms/bedrooms.

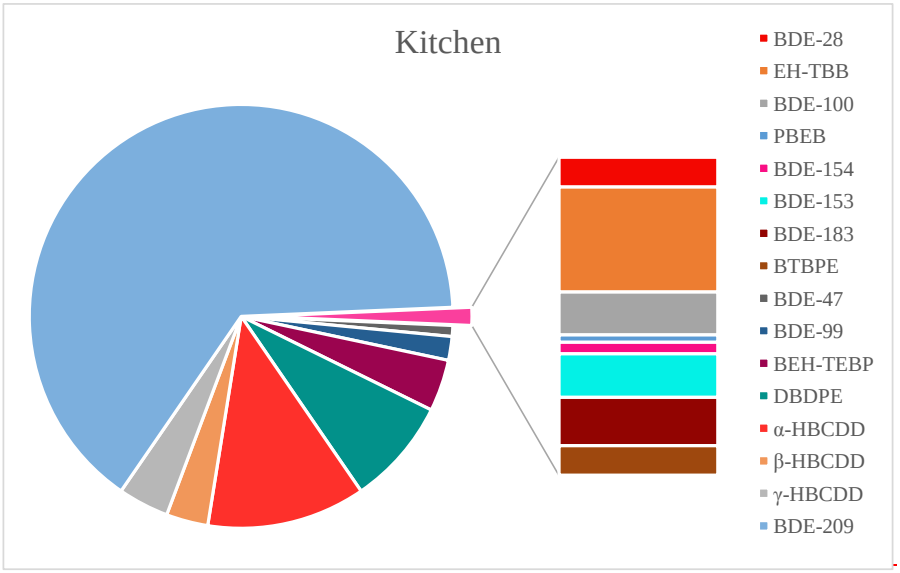
Table 2 Mean ranks of BFR concentration in carpeted living room/bedroom (CL), bare floor living room/bedroom (BL) and kitchen (K) of Kruskal-Wallis test

	CL	BL	K
BDE-28	29.93	27.75	29.68
PBEB	30.45	33.38	27.83

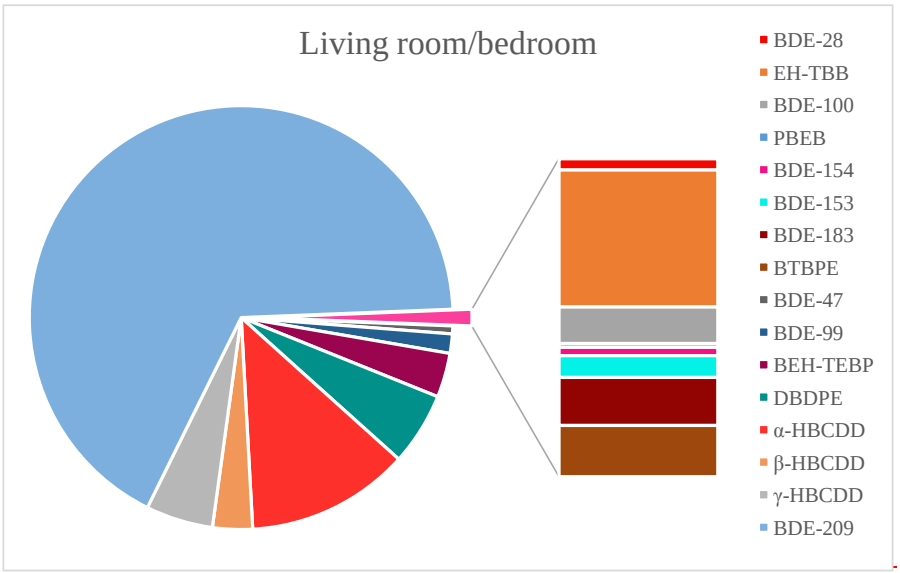
~~BDE-100~~	~~35.83~~	~~34.88~~	~~23.85~~
~~EH-TBB~~	~~35.58~~	~~33.25~~	~~24.45~~
~~BDE-154~~	~~34.65~~	~~31.31~~	~~25.58~~
~~BDE-153~~	~~34.03~~	~~31.06~~	~~26.07~~
~~BDE-183~~	~~35.33~~	~~25.38~~	~~24.05~~
~~BTBPE~~	~~35.70~~	~~35.75~~	~~23.70~~
~~BDE-47~~	~~35.88~~	~~33.63~~	~~24.15~~
~~BDE-99~~	~~34.38~~	~~35.19~~	~~24.73~~
~~BEH-TEBP~~	~~37.67~~	~~33.25~~	~~23.05~~
~~DBDPE~~	~~34.20~~	~~28.75~~	~~26.57~~
~~α-HBCDD~~	~~36.80~~	~~34.94~~	~~23.18~~
~~β-HBCDD~~	~~36.33~~	~~37.44~~	~~22.83~~
~~γ-HBCDD~~	~~33.67~~	~~31.31~~	~~26.23~~
~~BDE-209~~	~~34.95~~	~~34.31~~	~~24.58~~

In summary, this study reveals no evidence that the presence of carpet can explain the significantly elevated BFR concentrations in living room/bedroom dust compared to kitchen dust. We therefore investigated the reasons driving this difference further, by comparing the BFR profile in these two microenvironment categories. Figure 3 is drawn based on the median value of each compound from which it can be found that the composition profiles of kitchen and living room/bedroom dust are similar. To

further confirm this, we carried out a Wilcoxon test to compare the mass percentage of each compound in living room/bedroom and kitchen dust. To minimise the overwhelming impact of dominant components such as BDE-209, all target compounds were classified into three groups according to their concentration level as described in section 2.1. At the group level, the relative abundance of groups 1, 2, and BDE-209 were not significantly different between kitchen and living room/bedroom dust. Next, the percentage of each compound was calculated based on the total concentration of the group to which it was assigned. This approach revealed a significantly higher proportion ($p=0.001$) of BDE-28 in kitchens but higher proportions of BTBPE ($p=0.022$) and α-HBCDD ($p=0.035$) in living rooms/bedrooms. The proportion of β-HBCDD was also lower in kitchens, but at a significance level of $p= 0.056$. However, no significant difference was observed for γ-HBCDD ($p=0.600$). Notwithstanding these differences in the relative abundances of a small number of our target BFRs, there appears no clear evidence of major differences between the BFR profiles in kitchens and living rooms/bedrooms, which suggests that there are no major differences in source types between these two microenvironment categories.



(a)



(b)

Figure 3 Median BFR compositions in dust from kitchens (a) and living rooms/bedrooms (b)

As no specific source was identified as responsible for the higher BFR concentrations in dust from living rooms/bedrooms compared to those in kitchen dust, we propose instead that the cause is a generally higher BFR emission rate in living rooms/bedrooms. Although kitchens contain more putative sources, the rate at which BFRs may be emitted from these are influenced by factors such as material, volume and BFR content of sources, which can combine to obscure clear relationships between BFR contamination of dust and putative source counts. Moreover, our study only monitors a selection of BFRs, so it is possible that some FRs not targeted in our study are used in kitchen appliances. Further studies will be carried out to test this hypothesis. Another potential contributory factor may be that given the greater use of water for cleaning and cooking in kitchens, it is reasonable to assume that kitchens are more humid than living rooms/bedrooms. This may lead to greater water content on the surface of kitchen dust that may impede the sorption of BFRs from air.

4. Conclusions

Concentrations of 16 BFRs in dust from living rooms/bedrooms and kitchens from 30 UK homes are moderate compared with previous studies. Comparison of data for living rooms/bedrooms in this study with previous data for living room dust from the

same region of the UK in 2006-07, reveals concentrations of BDE-209 to have fallen significantly, while concentrations of DBDPE have risen. Concentrations of 13 out of our 16 target BFRs in kitchen dust are exceeded significantly by those in living room/bedroom dust. Comparison of BFR patterns in both microenvironment categories suggests that the sources of our target BFRs are similar in both. The higher concentrations in living rooms/bedrooms may be due to a combination of factors such as: an overall higher emission intensity of our target BFRs in living rooms and bedrooms, lower uptake of BFRs by dust in kitchens due to the higher humidity, and that kitchen appliances contain FRs different to those in living rooms/bedrooms and that are targeted in this study.

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Highlights

- First report of BFRs in domestic kitchen dust
- Levels of most BFRs significantly lower in kitchen than living room/bedroom dust
- Lower levels in kitchens may be due to more frequent cleaning and fewer BFR sources
- BDE-209 and DBDPE in house dust respectively decreased and increased since 2006-07

Graphical Abstract

Concentrations of "Legacy" and Novel Brominated Flame Retardants in matched samples of UK kitchen and living room/bedroom dust

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Abstract

Concentrations of polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDDs) and 5 novel brominated flame retardants (NBFRs) were measured in paired samples of kitchen and living room/bedroom dust sampled in 2015 from 30 UK homes. BDE-209 was most abundant (22–170,000 ng/g), followed by γ-HBCDD (1.7–21,000 ng/g), α-HBCDD (5.2–4,900 ng/g), β-HBCDD (2.3–1,600 ng/g), BDE-99 (2.6-1,440 ng/g), BDE-47 (0.4–940 ng/g), decabromodiphenyl ethane (DBDPE) (nd-680 ng/g) and bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEH-TEBP) (2.7-630 ng/g). The concentrations in kitchens and living rooms/bedrooms are moderate compared with previous studies. Concentrations of BDE-209 in living room/bedroom dust were significantly lower and those of DBDPE significantly higher ($p<0.05$) compared to concentrations recorded in UK house dust in 2006 and 2007. This may reflect changes in UK usage of these BFRs. All target BFRs were present at higher concentrations in living rooms/bedrooms than kitchens. With the exception of BDE-28, pentabromoethylbenzene (PBEB) and DBDPE, these differences were significant ($p<0.05$). No specific source was found that could account for the higher concentrations in living rooms/bedrooms.

Keywords

Brominated flame retardant; dust; kitchen; living room; bedroom

Highlights

- First report of BFRs in domestic kitchen dust
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1. Introduction

In order to comply with flame retardancy regulations in many jurisdictions, flame retardants (FRs) are widely added to textiles, plastics and building materials. At the current time, brominated flame retardants (BFRs) remain the most widely used class of FRs across the world, including: polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDDs), tetrabromobisphenol A (TBBPA), decabromodiphenyl ethane (DBDPE) and 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) (Alaee et al., 2003; Covaci et al., 2011). To date, a number of studies have reported potential adverse human health impacts for some BFRs, including thyroid toxicity (Meerts et al., 2000), neurotoxicity (Dingemans et al., 2011), reproductive toxicity (Meeker et al., 2009) and carcinogenicity (Darnerud, 2003). In addition, BFRs like PBDEs and HBCDDs are persistent, bioaccumulative and capable of undergoing long range environmental transport (Dickhut et al., 2012; Marvin et al., 2011; Wu et al., 2011; Zhang et al., 2009; Zhu et al., 2013). Owing to emissions from the myriad range of goods within which they have been incorporated, BFRs are ubiquitous in the environment and have been detected in nearly all abiotic environmental compartments (including water, air, soil, sediments, sewage sludge and dust) (Besis and Samara, 2012; Cristale et al., 2013; Gorga et al., 2013; Luo et al., 2013; Zhu et al., 2008). Such contamination has led to the widespread presence of

58 BFRs in biota such as insects, birds and mammals (Gaylor et al., 2012; Guo et al.,
59 2012; Jorundsdottir et al., 2013), as well as human tissues like hair, breast milk and
60 blood serum (Aleksa et al., 2012; Kim and Oh, 2014; Lee et al., 2013; Sjödin et al.,
61 2013; Tang et al., 2013).
62
63 Current understanding is that human exposure to PBDEs and HBCDDs occurs via a
64 combination of diet, indoor dust ingestion, dermal exposure, and inhalation of (largely
65 indoor) air (Abdallah et al., 2008; Besis and Samara, 2012; Daso et al., 2010;
66 Johnson-Restrepo and Kannan, 2009; Trudel et al., 2011). The suspected ecological
67 and human health risks of BFRs have driven international regulation of production
68 and use of some. Specifically, the commercial Penta- and Octa-BDE formulations
69 have been banned worldwide and listed under the UNEP Stockholm Convention on
70 persistent organic pollutants (POPs) since 2009 (Ashton et al., 2009). Moreover, the
71 commercial Deca-BDE formulation has also been restricted severely in Europe since
72 July 2008 (European Court of Justice, 2008), and is currently under active
73 consideration for listing under the Stockholm Convention. In addition, HBCDDs was
74 listed under Annex A of the Stockholm Convention in 2013 (Report of COP6,
75 Stockholm Convention, 2013). Such restrictions and bans on PBDEs and HBCDDs,
76 when coupled with the fixed or even increasing market demand for flame retardants is
77 inevitably leading to increased production of alternatives. While organophosphate
78 flame retardants (PFRs) are one alternative, others include the so-called “novel” BFRs

(NBFRs) such as: DBDPE, BTBPE, pentabromoethylbenzene (PBEB), bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEH-TEBP) and 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB). However, despite their perceived low cost and high performance, there exist substantial concerns about the environmental impacts of these and other NBFRs. Combined with the substantial remaining inventory of goods containing banned (or "legacy") BFRs and their persistence in the environment, this increased use of NBFRs means that environmental concerns about BFRs will remain an important issue for a considerable time.

With respect to the contamination of indoor dust with BFRs, most attention has been paid to house dust, with offices, cars and schools also featuring in some studies (Harrad et al., 2010). Within homes, the majority of studies have examined living room dust, with a smaller proportion studying bedrooms. To our knowledge however, no data exist about concentrations of BFRs in dust from domestic kitchens. This is a surprising omission, given that people may spend a substantial proportion of time in this microenvironment, and that kitchens contain a substantial number of goods such as microwave ovens, dishwashers, food processors, fridges, and freezers etc. that because their plastic components represent a fuel source in the event of fire, are likely to be flame-retarded.

Given this background, the objectives of this study are: 1. to report for the first time the concentrations of selected BFRs in kitchen dust; 2. to test the hypothesis that concentrations of BFRs in domestic kitchen dust exceed those in dust sampled simultaneously from other areas (living rooms/bedrooms) in the same houses, and 3. to test the hypothesis that restrictions on PBDEs in the EU, have led to reductions in concentrations of PBDEs in dust from UK living rooms, accompanied by concomitant increases in concentrations of NBFRs.

To achieve these objectives, we determined concentrations of 8 PBDEs (BDEs-28, 47, 99, 100, 153, 154, 183 and 209), 5 NBFRs (PBEB, EH-TBB, BTBPE, BEH-TEBP and DBDPE) and HBCDDs (α-, β-, γ-) in paired UK kitchen and living room (or bedroom) dust samples taken from 30 homes in the UK West Midlands conurbation in 2015. Data from kitchens are compared with those from living rooms and bedrooms; with those from living rooms/bedrooms in this study compared with those recorded in an earlier study conducted by our research group of dust from living rooms sampled in the UK West Midlands conurbation in 2006-07.

2. Material and methods

2.1 Sampling

In total, 30 homes from the West Midlands conurbation in the UK (of which

Birmingham is the main city) were sampled in 2015. For each home, a dust sample from the kitchen floor was collected with a floor dust sample collected from the living room in the same house for comparison. For the 11 homes in which the living room and kitchen were in the same room, dust in the bedroom was collected instead. For carpeted floor, dust was collected by vacuuming a 1 m^2 area for 2 min; while for bare floors, the vacuuming area and time were 4 m^2 and 4 min, respectively. More details about dust collection and storage protocols have been described in our previous studies (Harrad et al., 2008). An aliquot of 2-3 g pre-baked sodium sulfate vacuumed from a clean Al foil surface served as a field blank.

2.2 Chemicals

Native BDEs 77 and 128, ^{13}C-BTBPE, ^{13}C-BEH-TEBP, ^{13}C-BDE-209 and ^{13}C- α-, β-, γ-HBCDDs were used as internal standards. All standards above were purchased from Wellington Laboratories Inc. All solvents used (acetone, hexane, iso-octane and methanol) were HPLC grade.

2.3 Clean-up

First, 50-100 mg dust was accurately weighed and spiked with 25 ng internal (surrogate) standards. Hexane : acetone (3:1) (2 mL) was added to the sample, which was vortexed for 60 seconds, sonicated for 5 min and centrifuged at 2000 g for 2 min. After collecting the supernatant, the residues were subjected to the same extraction

process twice more. The combined supernatants were reduced in volume to ~ 2 mL under a gentle stream of nitrogen gas, before mixing with 3-4 mL 98% sulfuric acid. The mixture was then vortexed for 20 s followed by centrifugation at 2000 g for 5 min. The supernatant was then collected. To ensure complete transfer, the residue was rinsed with hexane (2 mL) three times. The combined supernatant was then reduced to incipient dryness under a gentle stream of nitrogen gas. The final concentrate was re-dissolved in 200 µL iso-octane prior to analysis of PBDEs and NBFRs by GC-MS. Following GC-MS analysis, solvent exchange from iso-octane to methanol was conducted to facilitate determination of HBCDDs on LC-MS-MS.

2.4 Analytical methods

2.4.1 GC-MS

A Thermo Trace 1310 gas chromatography interfaced with an ISQ single quadrupole MS equipped with a programmable-temperature vaporiser (PTV) was employed to conduct the analysis under electron capture negative ionisation (ECNI) mode. Two µL of purified sample extract were injected on a Thermo TG-SQC column (15 m×0.25 mm×0.25 µm). The injection temperature was set at 92 °C, held 0.04 min, ramp 700 °C/min to 295 °C. The GC temperature programme was initially 50 °C, held 0.50 min, ramp 20 °C/min to 240 °C, held 5 min, ramp 5 °C/min to 270 °C and then ramp 20 °C/min to 305 °C, held 16 min. Helium was used as a carrier gas with a flow rate of 1.5 mL/min for the first 22.00 min, then ramp 1.0 mL/min^2 to 2.5 mL/min, hold

13.00 min. The mass spectrometer was employed in selected ion monitoring (SIM) mode and the measured ions for each compound are listed in Table S1. Dwell times for each ion were 30 ms. The ion source and transfer line temperatures were set at 300 and 320 °C, respectively and the electron multiplier voltage was at 1400 V. Methane was used as reagent gas.

2.4.2 LC-MS-MS

A high-performance liquid chromatography (HPLC, LC-20AB, SHIMADZU) followed by electrospray ionisation and tandem mass spectrometry (ESI-MS-MS, API 2000, AB Sciex) was employed to measure the concentration of HBCDDs in this study. A Varian Pursuit XRS3 C18 analytical column (150 mm × 2 mm, 3 μm particle size) was used as stationary phase, and the mobile phase was a mixture of 1:1 water and methanol (phase A) and methanol (phase B). Elution started at 50 % phase B and then increased linearly to 100 % over 4 min, held isocratically for 5 min and then decreased to 65 % over 3 min, then returned to initial condition in 0.01 min and maintained for column regeneration for another 4 min, resulting in a total run time of 16 min. The flow rate and injection volume were 0.15 mL/min and 20 μL, respectively. The mass spectra were obtained in ESI (-) mode and data collected in MRM mode, with the parent and daughter ions for each compound listed in Table S2.

2.5 QA/QC

As a QA/QC check, one aliquot of SRM2585 (organics in house dust, NIST) was analysed for every 20 samples. Data obtained for these SRM analyses were very reproducible and in good agreement with the certified values (Table S3). One field blank was analysed every 10 samples. Most target compounds were not detected in blanks, or were detected at levels equivalent to a concentration in dust of below 1 ng/g, except BDE-209, which was detected in blanks at around 20 ng/g. Even for BDE-209, concentrations in blanks were always less than 5% of the concentrations detected in samples. Concentrations of each compound found in blanks are listed in Table S4 and are subtracted from the results of samples before further analysis of the data. The limits of detection for each target compound are listed in Table S5.

2.6 Statistical analysis

Statistical analysis of the data was conducted using Microsoft Excel 2013 to generate descriptive statistics, with all other statistical procedures conducted using IBM SPSS Statistics 19.0. As a first step, the distribution of concentrations of each compound within the dataset for each microenvironment category was evaluated using a Kolmogorov-Smirnov test. The results of this test and visual inspection of frequency diagrams together revealed both concentration and dust loading data in kitchen and living room to be log-normally distributed. Hence, concentrations and dust loadings

were log-transformed before performing t test comparisons. In all instances, where concentrations were below the detection limit, the concentration was assumed to equal half of the detection limit.

3. Results and discussion

3.1 Concentrations of BFRs

Table 1 lists minimum, maximum, and median concentrations of target BFRs in both kitchen and living room/bedroom dust in this study, while a boxplot (Figure 1) illustrates the concentration range and profile of target BFRs in our samples. Based on concentration range, the 16 BFRs targeted in this study may be categorised into three groups. BDE-28, PBEB, BDE-100, EH-TBB, BDE-154, BDE-153, BDE-183 and BTBPE belong to the first group, ranging from not detected to several tens ng/g with median concentrations lower than 10 ng/g. The second group contains BDE-47, BDE-99, BEH-TEBP, DBDPE and α-, β-, γ-HBCDDs, for which median concentrations range from 10 ng/g to hundreds ng/g and concentrations range from several ng/g to in excess of 1,000 ng/g. Finally, group 3 consists of BDE-209 only, for which concentrations range from several tens ng/g to more than 100,000 ng/g with a median value of nearly 1,000 ng/g. The concentration ranges and profiles obtained in this study are broadly consistent with previous studies as shown in Figure 2. This Figure plots median concentration values for exemplar previous studies (Abdallah et

al., 2008; Ali et al., 2013; Ali et al., 2012a; Ali et al., 2011; Ali et al., 2012b; Allen et al., 2013; Bjorklund et al., 2012; Brown et al., 2014; Carignan et al., 2013; Coakley et al., 2013; Dirtu et al., 2012; Dodson et al., 2012; Harrad and Abdallah, 2011; Harrad et al., 2008; Kalachova et al., 2012; Kang et al., 2011; Kefeni and Okonkwo, 2012; Nguyen Minh et al., 2013; Ni and Zeng, 2013; Shoeib et al., 2012; Stasinska et al., 2013; Tang et al., 2013; Thuresson et al., 2012; Vorkamp et al., 2011; Whitehead et al., 2013; Yu et al., 2012), alongside those detected in kitchen and living room/bedroom dust in this study (represented as red and black dots respectively). It can be seen that for most compounds, concentrations in this study are lower than previously reported, especially for BDEs-47, -154 and -153. This finding is not inconsistent with a reduction in the use of the Penta-BDE formulation since the early-mid-2000s. In contrast, concentrations of NBFRs, HBCDDs and BDE-209 recorded in this study are similar or even slightly higher than previously reported, which is consistent with the later introduction (or absence to date) of restrictions on use of these BFRs.

3.2 Is there evidence of temporal changes in BFR concentrations in living room/bedroom dust following restrictions on PBDE use?

To investigate the impact of recent restrictions on manufacture and use of PBDEs on concentrations of PBDEs and potential replacement NBFRs in UK indoor dust, we compared concentrations of individual PBDEs, BTBPE, and DBDPE in living room

and bedroom dust in our study, with those reported for 30 UK living room dust samples collected between 2006 and 2007 (Harrad et al., 2008). Before doing so, we first conducted a t-test comparison of log-transformed concentrations of our target BFRs in our living room and bedroom dust samples to verify the validity of aggregating these data in this context. This revealed no significant differences ($p>0.05$) between concentrations in living room and bedroom dust for any of our target BFRs. Consequently, we compared BFR concentrations in living room dust from 2006-07 with our combined data for living room and bedroom dust via a t test comparison of log-transformed concentrations in the two temporally-distinct sample groups. This revealed concentrations of most target BFRs to be statistically indistinguishable ($p>0.05$) between the two time periods. However, concentrations of BDE-209 and BDE-154 are significantly lower ($p<0.05$) and those of DBDPE and BDE-28 significantly higher ($p<0.05$) in this (later) study. While it is hard to rationalise the opposite trends in BDEs-28 and -154, and acknowledging the small sample numbers involved; the apparent decrease in concentrations of BDE-209, coupled with the corresponding increase of DBDPE, is not inconsistent with the 2008 introduction of restrictions on use of Deca-BDE in the EU (European Court of Justice, 2008), and reports that DBDPE is the main alternative to Deca-BDE (Covaci et al., 2011).

3.3 Are concentrations of BFRs higher in kitchen than living room/bedroom dust?

To test our hypothesis that concentrations of BFRs in kitchen dust will exceed significantly those in living area and bedroom dust from the same homes, we conducted a paired t test comparison between concentrations of individual BFRs in kitchen dust and those in living room and bedroom dust. This revealed concentrations for all but BDE-28, PBEB, and DBDPE to be significantly higher ($p<0.05$) in living room and bedroom dust compared to that from kitchens. Moreover, although not significant ($p>0.05$), a higher concentration was still observed for BDE-28, PBEB and DBDPE in living room/bedroom dust compared to kitchen dust. The higher concentrations observed in living rooms and bedrooms compared to the corresponding kitchens are not attributable simply to the respective number of putative sources in the two microenvironments. Kitchens in this study contained more potential sources, such as: fridges, microwave oven, washing machines, ovens, toasters, and curtains etc. than living rooms/bedrooms (which contained mainly carpets, TVs, computers, sofas, and curtains). Instead, it is plausible that the goods present in kitchens are treated with FRs other than the BFRs targeted in this study, in contrast to the goods found in living rooms/bedrooms. As carpet was absent from all the kitchens in this study, while being the most frequently reported putative source in living rooms/bedrooms (present in 21/30 of these microenvironments), we examined further whether the

presence/absence of carpets in this study could explain the differences between kitchens and living rooms/bedrooms. To do so, we classified the 60 dust samples into 3 groups: i.e. kitchen samples (K), bare floor living room/bedroom samples (BL) and carpeted living room/bedroom samples (CL) and subjected data on BFR concentrations (in this instance not log-transformed) in samples in each of these groups to a Kruskal-Wallis test. However, the mean ranks of BL and CL are very close (Table 2) and both are much higher than those of kitchen samples for most compounds. This result indicates that the presence of carpet does not significantly influence the concentrations of our target BFRs in living room/bedroom dust. Hence, the absence of carpet from kitchens does not account for the lower concentrations compared to living rooms/bedrooms.

In summary, this study reveals no evidence that the presence of carpet can explain the significantly elevated BFR concentrations in living room/bedroom dust compared to kitchen dust. We therefore investigated the reasons driving this difference further, by comparing the BFR profile in these two microenvironment categories. Figure 3 is drawn based on the median value of each compound from which it can be found that the composition profiles of kitchen and living room/bedroom dust are similar. To further confirm this, we carried out a Wilcoxon test to compare the mass percentage of each compound in living room/bedroom and kitchen dust. To minimise the overwhelming impact of dominant components such as BDE-209, all target

compounds were classified into three groups according to their concentration level as described in section 2.1. At the group level, the relative abundance of groups 1, 2, and BDE-209 were not significantly different between kitchen and living room/bedroom dust. Next, the percentage of each compound was calculated based on the total concentration of the group to which it was assigned. This approach revealed a significantly higher proportion ($p=0.001$) of BDE-28 in kitchens but higher proportions of BTBPE ($p=0.022$) and α-HBCDD ($p=0.035$) in living rooms/bedrooms. The proportion of β-HBCDD was also lower in kitchens, but at a significance level of $p= 0.056$. However, no significant difference was observed for γ-HBCDD ($p=0.600$). Notwithstanding these differences in the relative abundances of a small number of our target BFRs, there appears no clear evidence of major differences between the BFR profiles in kitchens and living rooms/bedrooms, which suggests that there are no major differences in source types between these two microenvironment categories.

As no specific source was identified as responsible for the higher BFR concentrations in dust from living rooms/bedrooms compared to those in kitchen dust, we propose instead that the cause is a generally higher BFR emission rate in living rooms/bedrooms. Although kitchens contain more putative sources, the rate at which BFRs may be emitted from these are influenced by factors such as material, volume and BFR content of sources, which can combine to obscure clear relationships between BFR contamination of dust and putative source counts. Moreover, our study

315 only monitors a selection of BFRs, so it is possible that some FRs not targeted in our
316 study are used in kitchen appliances. Further studies will be carried out to test this
317 hypothesis. Another potential contributory factor may be that given the greater use of
318 water for cleaning and cooking in kitchens, it is reasonable to assume that kitchens are
319 more humid than living rooms/bedrooms. This may lead to greater water content on
320 the surface of kitchen dust that may impede the sorption of BFRs from air.
321

322 # 4. Conclusions

323 Concentrations of 16 BFRs in dust from living rooms/bedrooms and kitchens from 30
324 UK homes are moderate compared with previous studies. Comparison of data for
325 living rooms/bedrooms in this study with previous data for living room dust from the
326 same region of the UK in 2006-07, reveals concentrations of BDE-209 to have fallen
327 significantly, while concentrations of DBDPE have risen. Concentrations of 13 out of
328 our 16 target BFRs in kitchen dust are exceeded significantly by those in living
329 room/bedroom dust. Comparison of BFR patterns in both microenvironment
330 categories suggests that the sources of our target BFRs are similar in both. The higher
331 concentrations in living rooms/bedrooms may be due to a combination of factors such
332 as: an overall higher emission intensity of our target BFRs in living rooms and
333 bedrooms, lower uptake of BFRs by dust in kitchens due to the higher humidity, and

that kitchen appliances contain FRs different to those in living rooms/bedrooms and that are targeted in this study.

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Table 1 Maximum (max), minimum (min) and median values of kitchen dust BFR concentration (K, ng/g), living room/bedroom dust BFR concentration (L, ng/g) and matched kitchen-living room/bedroom dust BFR concentration ratio (K/L)

	K			L			K/L		
	max	min	median	max	min	median	max	min	median
BDE-28	150	<0.2	1.2	55	<0.2	1.0	9.55	0.10	1.00
BDE-47	940	0.4	7.6	590	2.4	13	10.30	0.05	0.54
BDE-99	1400	2.6	17	930	4.0	33	15.37	0.06	0.46
BDE-100	320	<0.2	1.7	140	0.7	3.2	7.23	0.03	0.40
BDE-153	410	0.1	1.7	170	<0.4	1.9	10.02	0.01	0.58
BDE-154	180	<0.4	0.4	60	<0.4	0.7	8.64	0.03	0.52
BDE-183	29	<1.0	1.9	120	0.6	4.2	4.57	0.02	0.46
BDE-209	32000	22	590	170000	170	1500	3.92	0.03	0.33
PBEB	25	<0.2	0.3	15	<0.2	0.4	4.45	0.06	0.84
EH-TBB	290	<0.2	4.1	450	<0.2	12	2.85	0.01	0.37
BTBPE	10	<1.0	1.2	97	<1.0	4.5	5.29	0.02	0.44
BEH-TEBP	420	2.7	36	630	7.8	75	2.35	0.05	0.36
DBDPE	450	<9.2	74	680	21	120	12.09	0.03	0.72
α-HBCDD	3800	5.2	110	4900	75	280	2.88	0.05	0.37
β-HBCDD	1100	2.3	29	1600	6.4	67	1.86	0.08	0.41
γ-HBCDD	13000	1.7	35	21000	14	110	34.85	0.003	0.37

Table 2 Mean ranks of BFR concentration in carpeted living room/bedroom (CL), bare floor living room/bedroom (BL) and kitchen (K) of Kruskal-Wallis test

	CL	BL	K
BDE-28	29.93	27.75	29.68
PBEB	30.45	33.38	27.83
BDE-100	35.83	34.88	23.85
EH-TBB	35.58	33.25	24.45
BDE-154	34.65	31.31	25.58
BDE-153	34.03	31.06	26.07
BDE-183	35.33	25.38	24.05
BTBPE	35.70	35.75	23.70
BDE-47	35.88	33.63	24.15
BDE-99	34.38	35.19	24.73
BEH-TEBP	37.67	33.25	23.05
DBDPE	34.20	28.75	26.57
α-HBCDD	36.80	34.94	23.18
β-HBCDD	36.33	37.44	22.83
γ-HBCDD	33.67	31.31	26.23
BDE-209	34.95	34.31	24.58

Table 1 Maximum (max), minimum (min) and median values of kitchen dust BFR concentration (K, ng/g), living room/bedroom dust BFR concentration (L, ng/g) and matched kitchen-living room/bedroom dust BFR concentration ratio (K/L)

	K			L			K/L		
	max	min	median	max	min	median	max	min	median
BDE-28	150	<0.2	1.2	55	<0.2	1.0	9.55	0.10	1.00
BDE-47	940	0.4	7.6	590	2.4	13	10.30	0.05	0.54
BDE-99	1400	2.6	17	930	4.0	33	15.37	0.06	0.46
BDE-100	320	<0.2	1.7	140	0.7	3.2	7.23	0.03	0.40
BDE-153	410	0.1	1.7	170	<0.4	1.9	10.02	0.01	0.58
BDE-154	180	<0.4	0.4	60	<0.4	0.7	8.64	0.03	0.52
BDE-183	29	<1.0	1.9	120	0.6	4.2	4.57	0.02	0.46
BDE-209	32000	22	590	170000	170	1500	3.92	0.03	0.33
PBEB	25	<0.2	0.3	15	<0.2	0.4	4.45	0.06	0.84
EH-TBB	290	<0.2	4.1	450	<0.2	12	2.85	0.01	0.37
BTBPE	10	<1.0	1.2	97	<1.0	4.5	5.29	0.02	0.44
BEH-TEBP	420	2.7	36	630	7.8	75	2.35	0.05	0.36
DBDPE	450	<9.2	74	680	21	120	12.09	0.03	0.72
α-HBCDD	3800	5.2	110	4900	75	280	2.88	0.05	0.37
β-HBCDD	1100	2.3	29	1600	6.4	67	1.86	0.08	0.41
γ-HBCDD	13000	1.7	35	21000	14	110	34.85	0.003	0.37

Table 2 Mean ranks of BFR concentration in carpeted living room/bedroom (CL), bare floor living room/bedroom (BL) and kitchen (K) of Kruskal-Wallis test

	CL	BL	K
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BDE-154	34.65	31.31	25.58
BDE-153	34.03	31.06	26.07
BDE-183	35.33	25.38	24.05
BTBPE	35.70	35.75	23.70
BDE-47	35.88	33.63	24.15
BDE-99	34.38	35.19	24.73
BEH-TEBP	37.67	33.25	23.05
DBDPE	34.20	28.75	26.57
α-HBCDD	36.80	34.94	23.18
β-HBCDD	36.33	37.44	22.83
γ-HBCDD	33.67	31.31	26.23
BDE-209	34.95	34.31	24.58

Figure 1

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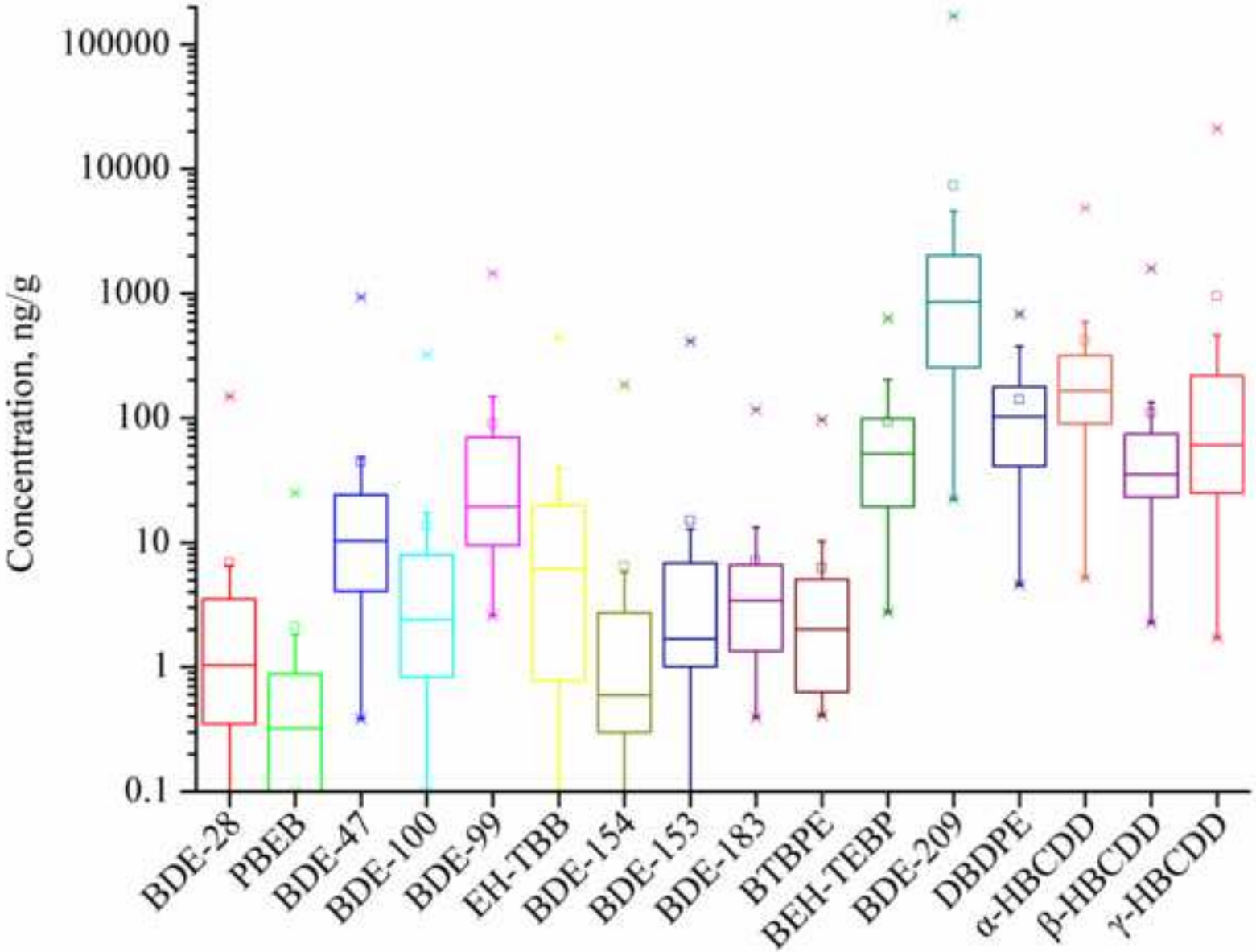

Figure 2

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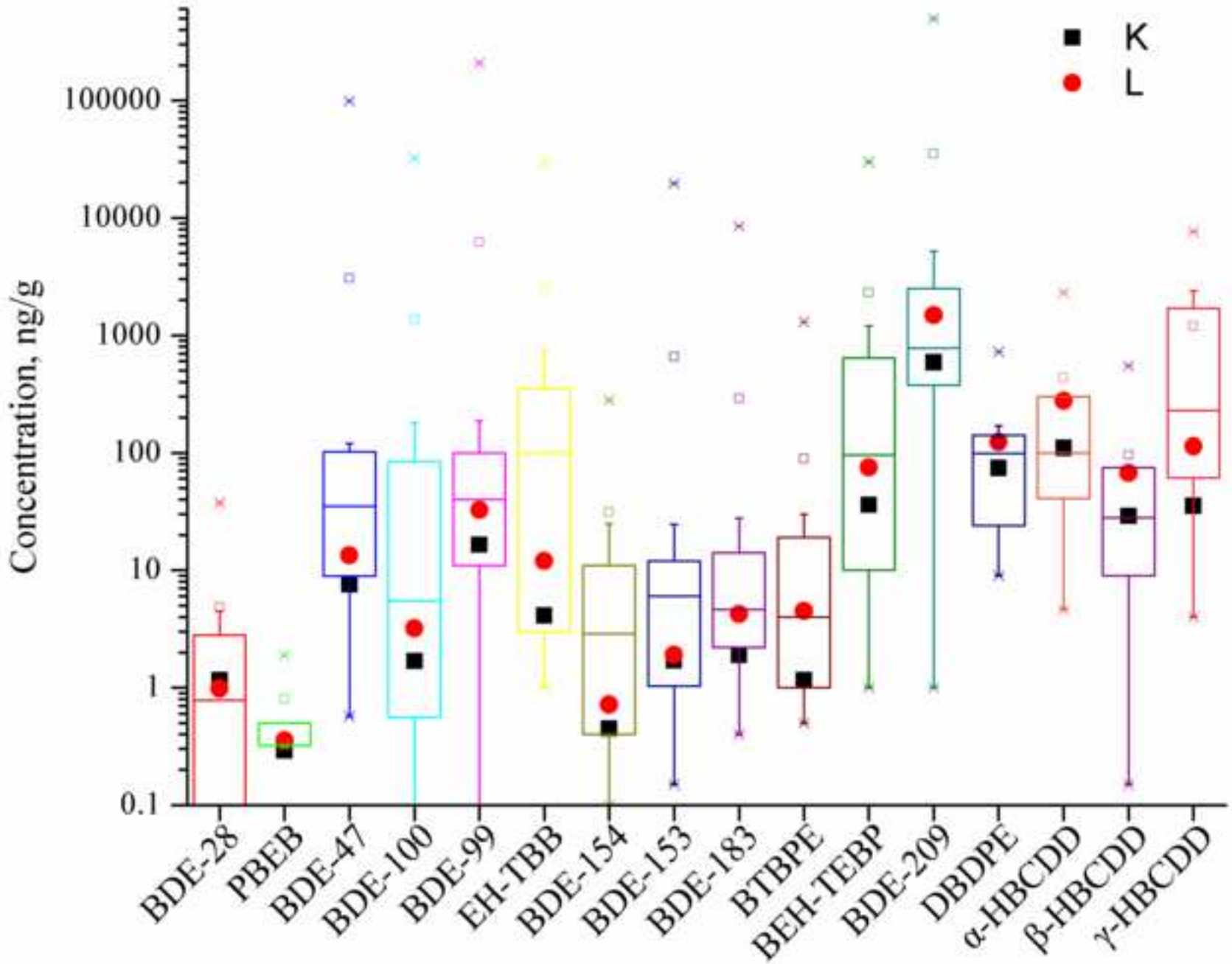
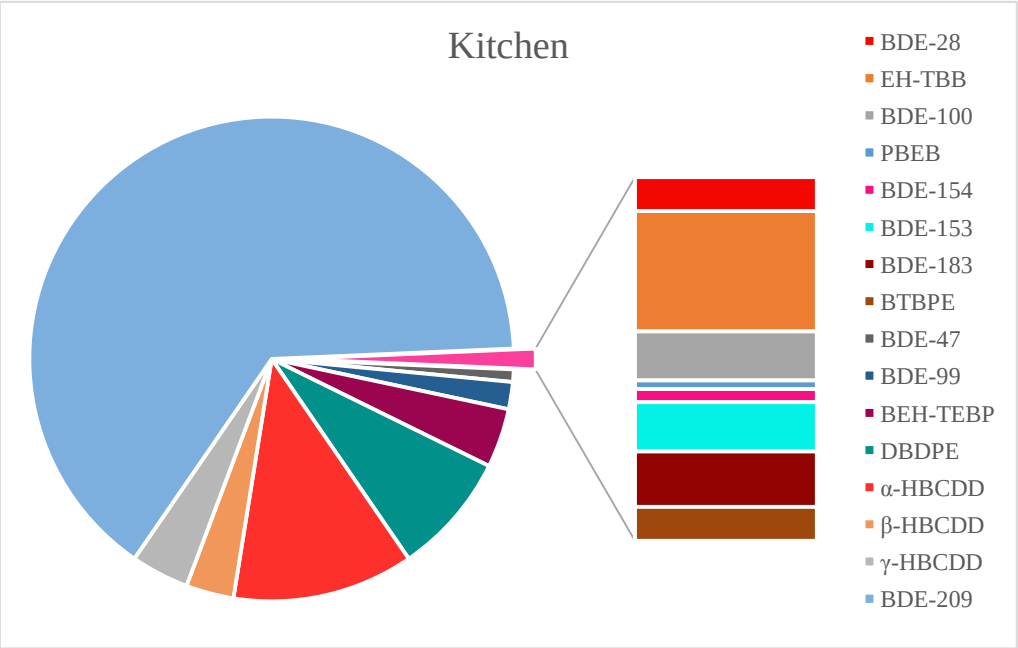
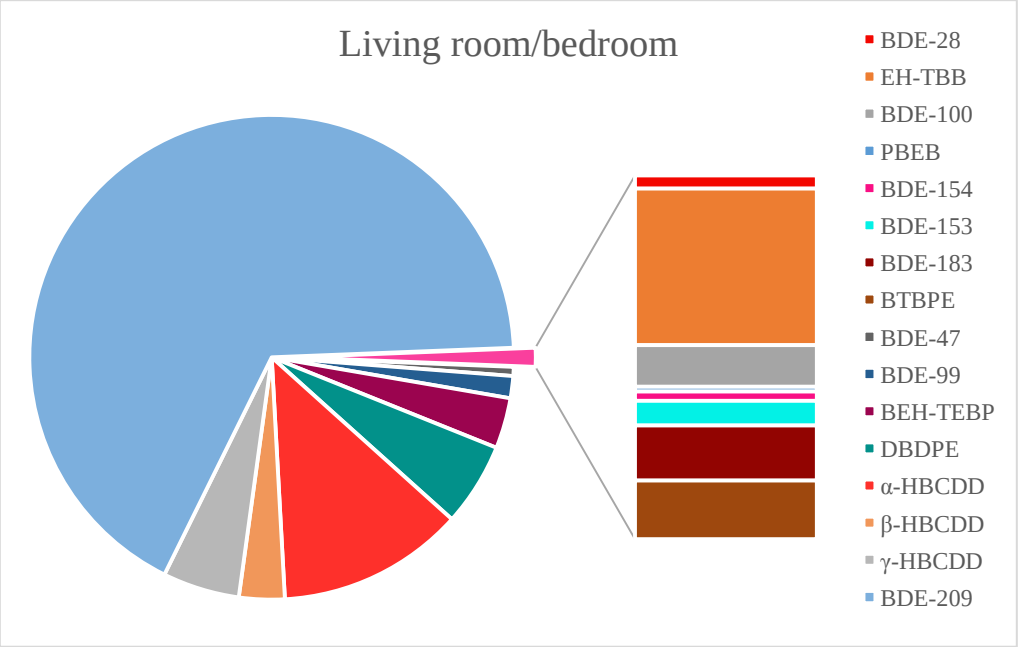


Figure 3


Kitchen
BDE-28
EH-TBB
BDE-100
PBEB
BDE-154
BDE-153
BDE-183
BTBPE
BDE-47
BDE-99
BEH-TEBP
DBDPE
α-HBCDD
β-HBCDD
γ-HBCDD
BDE-209

(a)


Living room/bedroom
BDE-28
EH-TBB
BDE-100
PBEB
BDE-154
BDE-153
BDE-183
BTBPE
BDE-47
BDE-99
BEH-TEBP
DBDPE
α-HBCDD
β-HBCDD
γ-HBCDD
BDE-209

(b)

Figure captions

Figure 1 Concentration range of BFRs in this study

Figure 2 Median concentrations of target BFRs in this study (K, kitchen; L, living room/bedroom) compared to the range of medians reported in selected previous studies

Figure 3 Median BFR compositions in dust from kitchens (a) and living rooms/bedrooms (b)

Supplementary Material

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